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MASS SPECTROMETRY, INFRARED SPECTROSCOPY AND NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY*

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1. INTRODUCTION

The technique of chromatography introduced in the previous chapter is an excellent method for purifying and isolating substances, but for these isolated materials it provides no information with regard to their material type (including molecular structures).

MS (Mass Spectrometry), IR (Infrared Spectroscopy), NMR (Nuclear Magnetic Resonance Spectroscopy), UV (Ultraviolet Spectrophotometry), Raman Spectroscopy, etc. are the analytical methods used to identify unknown compounds according to the resonances exhibited by the molecules. The responses that these compounds exhibit are recorded as spectra. The spectra provide information related to molecular structure on the horizontal axis, while the vertical axis shows its intensity. By interpreting these spectra, the identification and structures of the compounds can be deduced.

In Japan these analytical methods came into use in an orderly manner after the Second World War, and with the developments in greater sensitivity and greater resolution, and the development of new methods for

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measuring various types of samples, more accurate information can now be obtained. At present, these methods are essential for analyzing organic compounds in many different fields.

From among these instrumental analytical methods, this chapter will give an introductory description of the most widely used of these methods, in particular, the principles, the measurement methods and examples of MS, IR and NMR.

2. MS

2.1 History of MS

In 1910 Thomson succeeded for the first time in determining the masses of various atomic and molecular ions which were generated by discharge, and thus opened the way to MS.[1,2] Also, in 1912 he discovered a neon atom with a mass of 22 in addition to the mass 20 atom, that is, he discovered the presence of a stable isotope.[3] This was the first time that it was shown that non-radioactive elements have isotopes.

In 1910 Aston, a disciple of Thomson, built an instrument with a resolving power of about 130.[4]

After these initial works, MS was used for uncovering isotopes of the elements and for measuring the ratio of isotopes, but in the period 1940-1945 the work of Washburn, *et al.*[5-9] and Hipple[10] made improvements to the mass spectrometer so it could be used for qualititative and quantitative analysis of organic compound mixtures consisting mainly of hydrocarbons, and then this was rapidly followed by applications to analytical chemistry.

At present, instruments are available which have a maximum resolution of greater than 100,000 and maximum molecular weights of greater than 100,000 can be determined.

2.2 Principles and Characteristics of MS

Figure 1 shows the flow chart for MS. When a high energy source such as an electron beam is applied to a thermally vaporized sample molecule in a high vacuum, an electron in the molecule (bonded electron or non-bonded electron) is ejected to generate a cation radical of the molecule (M^+, parent ion). The parent ion breaks down further to produce many more ions, which are called fragment ions. When an electric field or magnetic field is applied to these ions, they are separated according to the ratio (m/z) of the mass (m) to the charge (z), and then the relative strengths of these separated ions are measured. Thus, it can be said that MS is a technique in which the mass of a substance is not directly measured on a balance, but rather the mass information is obtained indirectly by using the electrical properties of the charged particles.

The result obtained is called a mass spectrum, which shows the mass (m/z) on the horizontal axis (abscissa) and the relative strength on the vertical axis (ordinate).

The following information can be obtained from a mass spectrum.

(1) An accurate molecular weight can be obtained.

From the mass number of the parent ion peak, the molecular weight of the sample can be determined accurately to the nearest whole number. Using p.25
a high-resolution mass spectrometer (resolution of several 10,000's or greater) differences in mass to 3 decimal places (milli-mass) can be detected.

(2) The compounds can be identified.

When the structure of the sample compound is postulated, by comparing the spectrum to that of the standard compound, it can be identified.

(3) The structures of unknown compounds can be inferred.

From the manner in which the fragment ions are formed (fragmentation), the molecular structure can be inferred. In reality the interpretation of the frament ion pattern alone is not easy, and so information from IR or NMR, etc. are also used for reference.

(4) The isotope ratios can be measured.

The ratio of isotopes can be measured directly from the mass spectrum. Also, for an atom that has isotopes, from the values of the isotopic ratio and the pattern in the mass spectrum, the presence and the number of atoms of this element can be deduced.

2.3 MS Instrument

As shown in Figure 1, the basic functions of the instrument are ionization, separation of the masses (dispersion and focussing), and detection.

2.3.1 Ionization Methods and Ion Sources

The most widely used ionization method is EI (Electron Impact), but because the parent ions generated by EI have high internal energies, subsequent fragmentations occur to produce a large number of lower-mass ions, and in some cases the parent ion peak cannot even be observed. On the other hand, for the analysis of thermally-unstable non-volatile compounds or complex mixtures, etc., an ionization method is required which produces much more distinct parent ions by ionizing the sample without volatilization. Recently, soft ionization methods, which meet these requirements, have been developed.

The common ionization methods in use today are listed in Table 1. In p.26
addition to the ones in Table 1, there are methods known that use laser beams[11] or excited atoms as an ionization method[12], etc. From among these

ionization methods, the appropriate method is chosen for use depending on the type of sample, the form and the purpose of use.

2.3.2 Mass Separation

There are many methods in use for separating the masses, but the common ones in use are the following.

(a) Single Focussing Type

This is the type which uses a magnetic field only for focussing. Figure 2 shows a schematic diagram of a single focussing mass spectrometer. An ion (mass of m, charge of z) generated at the ion source is accelerated by an accelerating voltage **V** to a velocity **v**, and the kinetic energy gained is defined by the following equation.

$$1/2\ mv^2 = zV \quad \ldots\ldots\ldots\ldots\ldots \quad 1$$

Next the ion enters a magnetic field with a magnetic strength H, where the orbit of the ion is a curve with a radius r. At this time the centrifugal force on the ion is in balance with the magnetic field strength.

$$mv^2/r = Hzv \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad 2$$

If **v** is removed from both equations **1** and **2**, the following equation is obtained.

$$m/z = r^2H^2/2V \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad 3$$

From equation **3**, because r is a constant value due to the construction of the instrument, then with either H or **V** fixed, the other is varied over the scan range, and then ions of different m/z can be collected at the detector in sequential order.

(b) Double Focussing Type

The above type of instrument (single focussing) cannot be used when the generated ions have a wide initial-velocity distribution or when milli-masses need to be measured. In these cases the method used is one in which ions of given energies are first removed with an electric field, and the other ions are then separated in a magnetic field according to m/z, that is, a double focussing type mass spectrometer is used. Figure 3 shows a schematic diagram of the double focussing mass spectrometer.

Compared to the single focussing type, because the ion beam is screened by the electric field, the ion beam strength is decreased, but the focussing by the magnetic field produces good images, and thus high resolution can be obtained.

At present the double focussing mass spectrometer is much more widely used than the single focussing type.

(c) Other Types

Other types of mass separation used are the quadrupole type, time-of-flight type, ion cyclotron type, etc.

The quadrupole type makes use of the fact that when the ions enter between two pairs of parallel electrodes which have both direct current and high frequency alternating current applied, the ions of those m/z which resonate at certain wavelengths pass through, and so this instrument can be made in a compact size.

For the time-of-flight type, the ions are accelerated by a pulse voltage and then when they enter the region of no electricity, the ions of smaller m/z travel faster, and this occurs repeatedly for each pulse. An instrument of this type can be small, and a wide range of masses can be measured in a short time, of the order of a few μ-seconds.

In the ion cyclotron type, when the ions in a circular motion in a homogeneous magnetic field are subjected to a high frequency electric field, the ions of certain m/z are accelerated due to resonance and the radius of their circular motion becomes larger. This type of instrument also gives high resolution.

2.3.3 Detection

In the past, Faraday tubes and photographic plates were used, but in recent times secondary electron multiplier tubes are the ones in greatest use.

The secondary electron multiplier tube is a device in which a small number of mass-separated ions strike a metal surface to discharge many secondary electrons, and this occurs repeatedly for amplification, and so this device contains 10-20 metal plates.

2.4 Chemical Compounds and Mass Spectra

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2.4.1 Deducing the Molecular Formulae

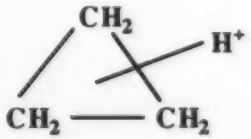
With ^{12}C = 12.0000, the mass weight of each element is not a precise integer, but the values are a small fraction off. For example, CO_2, C_3H_8, and N_2O all have a parent ion m/z = 44, but the actual values are 43.9988, 44.0635 and 44.0128, respectively.[13] Therefore, using a high resolution instrument, the molecular formula of an unknown compound can be deduced.

On the other hand, a similar treatment can be carried out on the ratio of natural isotopes. Table 2 shows the isotope ratios of the main elements.[13] Now, suppose that the m/z and relative strength ratios were obtained from a mass spectrum as shown in Table 3. Several element combinations can be considered for m/z = M = 92, but because of a variety

of reasons[footnote 1], the possibilities can be narrowed down to the molecular formulae shown in Table 4. With regard to these molecular formulae, with M given a value of 100, the relative ratios of M+1 and M+2 were obtained, and are listed in Table 4. The best fit to the actually measured values of Table 3 is C_7H_8, and so this sample is presumed to be toluene. However, this method is only effective when a strong parent ion peak is observed. It is convenient to use the list given by Beynon[14] for selecting a molecular formula which best fits the specific sample and the amount of isotopes.

2.4.2 Fragmentation Pattern

The fragmentation pattern begins from the parent ion, and a characteristic pattern is observed according to the type of sample compound. Figure 4 shows the mass spectrum[15] of *n*-nonane (C_9H_{20}, M=128). In the case of saturated hydrocarbons, the C-C bonds are cleaved and C_nH_{2n+1} (for *n*-nonane, 29, 43, 57, ..., 113) become the major peaks, and are normally followed by the C_nH_{2n-1} and C_nH_{2n} peaks. The fragment ion m/z=43 is stabilized by the formation of a protonated cyclopropane structure, and it is usually the strongest peak.



If information on other compounds, with regard to type and further details, are needed, there are a number of reference books available.[16-21]

2.5 Combination with Chromatography

Starting with molecular weights, MS provides much information on the

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[footnote 1] Because the M+2 peak intensities are very weak, halogens or sulfur are not included. Also, it can also be determined by the nitrogen rule.

structure of compounds, but because it does not have a means of separating mixtures, it is not suitable for analyzing mixtures. Thus, an effective way of analyzing mixtures is to use MS in combination with chromatography, one of the separation methods.

2.5.1 GC/MS (Gas Chromatography/Mass Spectroscopy)

The GC/MS analyzer is an instrument in which the GC column outlet is connected to the MS sample inlet. Because of the improvements in the interfaces connecting GC with MS, the high-speed measurement of MS, and the establishment of data handling techniques, GC/MS has become a very useful analytical method.

When a packed column is used in the GC, in order to maintain the vacuum of the MS, an interface such as a jet separator, etc. is used, and the carrier gas (He) coming out of the column is removed; then after the sample is concentrated, it is introduced into the MS.

In the case of a capillary column, because the He flow volume is low p.28 (a few ml/min), an interface is not required, and so the column outlet is connected directly to the MS ionization chamber. Because of this, MS measurements become possible without a decrease in the GC separation efficiency.

2.5.2 LC/MS (Liquid Chromatography/Mass Spectroscopy)

Investigations have begun on using LC in combination with MS which can analyze those compounds which are thermally unstable or non-volatile, that is, those which cannot be analyzed by GC. In the case of LC/MS, the mobile phase of LC is a liquid, and work has been started to develop an interface which suppresses the flow of large volumes of liquid into the MS so that the vacuum can be maintained.

Table 5 shows the typical LC/MS interfaces which have been developed up to the present. The frit-FAB method in Table 5 is one in which a few µl/min volume from the LC eluent is directly placed on the frit, and the FAB ionization is carried out by using this frit as the FAB target. Using this method means than continuous sample introductions are possible, and so a wide range of samples can be measured.

2.5.3 SFC/MS(Supercritical Fluid Chromatography/Mass Spectrometry)

With SCF there is no need to volatilize the mobile phase like there is with LC, and so its combination with MS is considered to be more favorable than with LC.

Although the number of reports on the use of SFC/MS are still quite limited, there have been reports on the analyses of the extracts of carbon black[34] and of oil industry related substances[35], and future developments are expected.

2.6 MS/MS

Basically, the MS/MS instrument is one in which two mass spectrometers are directly connected, but many types are possible using combinations of electrical and magnetic fields and/or quadrupoles.

The ionized sample is mass separated by the first stage MS. Here a specific separated ion (for example the parent ion) is passed through a collision chamber filled with a rare gas, etc., to produce further fragmentation. The ions fragmented in the collision chamber are mass-separated in the second-stage MS and the mass spectrum is obtained. Because this mass spectrum gives ion species (daughter ions) originating from the ion separated in the first-stage MS, it is very helpful in molecular structure determination. Also, similar to the separation

techniques such as GC or LC, etc., this can also be used for the analysis of mixtures.

2.7 Application to the Oil Industry[36]

2.7.1 Type Analysis

Type analysis is a method in which analyses are carried out according to the compound type, such as the quantity of paraffin or the quantity of aromatics in the sample. The type analyses of hydrocarbons from oil distillates (gasoline, heating oil, light oil) by MS using the EI ion source is regulated by several test methods[37] by ASTM.

For type analyses using high-resolution mass spectrometry instruments, there are reports[38-42] on the type analyses of sulfur, oxygen and nitrogen compounds in addition to saturated and aromatic hydrocarbons found in coker gas oil, shale oil, etc.

The type analyses and molecular weight distributions, etc., obtained by using soft ionization methods such as FD, FI, etc. on gasoline distillates or heavy oils, etc. have also been reported.[43-51]

2.7.2 Analysis of Additives

MS by a soft ionization method has been used for the analysis of the libricant additive Zn·DTP (Zinc dialkyl dithio-phosphate).[52]

2.7.3 Analysis of Sulfur Compounds

Aromatic compounds containing sulfur in the residual oils of FCC have been separated by GC/MS according to the number of rings, and 65 types of sulfur compounds have been quantitatively determined.[53]

2.7.4 Analysis of Nitrogen Compounds

The identification and quantitative determination of polycyclic aromatic nitrogen compounds in crude oil or liquefied coal have been carried out by using GC/MS or MS/MS.[54-56]

3. IR

3.1 History of IR

In 1800 Herschel[57] discovered infrared radiation for the first time. In 1892 the first paper showing the relationship between the chemical structure of a molecule and the infrared spectrum was reported by Julius.[58] In the following several decades the fundamentals of IR with regard to molecular structure were established, such as that an organic compound with a certain functional group exhibits an infrared absorption at a certain wavelength, etc., but with regard to analytical chemistry, it was still quite undeveloped. This was so because the handling of the early instruments was not easy, and using them was tedious and time consuming, and moreover, because a continuous spectrum could not yet be recorded.

However, with the rapid developments in IR detection methods, etc., along with the advances in electronic tubes, from around the time of the Second World War infrared spectra could now be measured quite simply and moreover rapidly, and applications to analytical chemistry spread rapidly. In particular, in 1959 a simple instrument model became commercially available, and so its use became more widespread.

In the 1970's, because of the rapid advances in small-sized computers p.29 and a decrease in their cost, FT-IR (Fourier Transform Infrared Spectroscopy) also became readily available. This method is used in the same areas as previously, but the applications of IR have been expanded further to a much wider area, and is contributing to high-level research activities such as for micro-sample analyses and surface analyses, etc.

3.2 Principles and Properties of IR

When a substance is irradiated with an electromagnetic wave (light), the substance absorbs at a certain wavelength of the radiation according to its molecular structure, and the energy level of the molecule goes from the ground state level, which is specific to the molecule, to an excited state. The energy of the molecule is considered to be the sum of the various energies, while the absorption of infrared radiation (wavelength of 2.5-25 μ, wavenumbers of 400-4000 cm^{-1}) is mainly based in the vibrational energy region.

The IR method makes use of this phenomenon to measure the infrared radiation absorptions to produce the spectrum, which is used to interpret the molecular structure.

The obtained result is called the infrared spectrum or IR spectrum, with the wavenumber [cm^{-1}] (or wavelength [μ]) on the horizontal axis, and the transmittance ratio [%] on the vertical axis.

The following can be determined from the infrared spectrum.

(1) The sample can be identified.

In cases where the identity of the sample substance can be postulated, the identification and confirmation can be carried out by comparing the spectrum with the known infrared spectrum.

(2) The structural features of unknown compounds can be obtained.

The main structural features which can be obtained from the infrared spectrum are multiple bonds and functional groups, but furthermore, one can also ascertain cis-trans isomers, the position of substrates on rings, hydrogen bonding and chelation, etc., and these findings can be used to determine the molecular structure. However, in general, it is difficult to determine the structure by using only the infrared spectrum, and so the

determination is usually carried out by also using information from other sources such as from MS, NMR, elemental analysis, UV, etc.

(3) Quantitative Analyses can be carried out.

Measurements to evaluate purity or the component ratios of mixtures can be carried out, and these measurements in turn can be used to determine reaction rates, etc.

In comparison to the MS and NMR instruments, an IR instrument is inexpensive to purchase, and also because it does not require special techniques for carrying out the measurements, the number of IR instruments in use is quite large. Also, because the electromagnetic-wave irradiation energy impinging on the sample is quite low, there is little danger of altering the nature of the sample substrate, and the sample can be recovered unchanged.

3.3 IR Instruments

If IR instruments are classified according to the optical system used, there are 2 broad classifications, and they are the dispersion type which uses a diffraction grating, and the interference type used in FT-IR. Also, there are 2 types if classified according to the number of optical paths for the infrared radiation, the single-beam type and the double-beam type. In the single-beam type the beam from the radiation source has a single optical path, while in the double-beam type the beam from the radiation source has two optical paths in which the effects of the background are corrected.

3.3.1 The Dispersion Type

The basic configuration of the dispersion IR instrument is shown in Figure 5. The infrared radiation from the radiation source is split into two by the reflection mirror, and then one beam irradiates the sample in

the sample cell while the other beam irradiates the control sample. The beams which pass through the sample and the control are separated according to wavenumber by the diffraction grating in the monochromator section. In the detection section the transmittance at each wavenumber is measured, and then recorded as the infrared spectrum.

Although it depends on the instrument used, it requires about 5-10 minutes to analyze the complete infrared range of wavenumbers.

3.3.2 The Interference Type

Figure 6 shows the basic composition of an FT-IR instrument. The FT-IR instrument components can be divided into 3 main sections: the optical system which extends from where the infrared radiation leaves the radiation source up to where it enters the detector, the analog signal treatment system, which is from the detector to the A/D converter, and the digital signal treatment system which comes after the A/D converter. In addition to these, there is the electrical system which controls the interferometer, etc.

Figure 7 shows a schematic diagram showing the sections up to the interferometer. When the infrared radiation (a in the Figure) from the radiation source passes through the sample, absorption occurs at certain wavenumbers based on the molecular structure of the sample material. The beam which passes through the sample (b in the Figure) is split into two by the beam splitter, with one part going to the fixed mirror, while the other passes through and is reflected by the moving mirror; then they converge again at the beam splitter, and because of differences in the optical paths, there is a phase shift, and the resulting radiation is an interference wave (interferogram, c in the Figure). For measuring the motion of the moving mirror, a He-Ne gas laser is used to make corrections.

Because of this, the wavenumber values in the measured infrared spectrum have an accuracy of greater than 7 figures. In Figures 6 and 7, the position of the sample is before the interferometer, but because the same interference waves can be obtained by placing the sample after the interferometer, the samples are usually positioned after the interferometer, except for samples that are fluorescent.

After passing through the sample, the interference wave radiation p.30
emanating from the beam splitter is sampled at given intervals by the A/D converter and accumulated as digital signals. The digital values of the interference waves are Fourier transformed by the computer to obtain the absorbances at each wavenumber, and the infrared spectrum is obtained after converting these absorbances to transmittance values.

For FT-IR, with one scan of the moving mirror of Figure 7, the interference wave obtained contains the wavenumbers of the entire infrared region, and so the measuring time is very much reduced (of the order of seconds). Also, because scattering of the infrared radiation is not required like in the case of the dispersion type, the sample receives ample infrared radiation energy, and a high-sensitivity analysis is possible. In addition to these features, FT-IR has the following properties.

-It has high resolution.

-The wavenumber accuracy and wavenumber reproducibility is very high.

-By increasing the number of measurements (scans) and accumulating them, the S/N can be improved.

-By interfacing to a computer, spectral interpretations are possible.

Because of these properties, the following types of measurements, which could not have been carried out with the dispersion type, are now possible.

(1) Measurement of fluorescing samples.

(2) Measurement of dilute or micro sample amounts.

(3) Measurement of dark colored samples.

(4) Analysis of surfaces.

(5) Difference spectral measurements.

(6) Following changes with time (kinetic measurements).

3.4 The Measurement Methods

p.31

Table 6 shows the typical methods of measuring IR. From among those in Table 6, the appropriate method can be selected according to the type of sample. Details of the measurement methods are given in a reference publication.[59]

In addition, there are GC/FT-IR and LC/FT-IR systems in use which have the GC or LC, used for sample separations, placed ahead of the FT-IR which carries out high-sensitivity and high-speed measurements.

3.5 Measurement Example

Figure 8 shows the infrared spectra of *o*-xylene, *m*-xylene and *p*-xylene.[60] Because the mass numbers of all three compounds are the same, MS cannot be used to tell them apart. However, each of these compounds can be identified by IR according to the patterns in the 600 - 900 cm^{-1} region.

Thus, IR is especially effective for identifying isomers.

For the interpretation of infrared spectra, a number of references[16,61-63] can be consulted.

4. NMR

4.1 History of NMR

The first NMR signals were observed independently in 1946 by two groups of physicists. Bloch *et al.*[64] of Stanford University observed the ^{1}H (proton) signal of water, while Purcell *et al.*[65] of Harvard University observed the proton signals of paraffin wax. For these discoveries, Bloch and Purcell shared the Nobel Prize in 1952.

Chemists began paying attention to NMR following the reports[66-68] around 1950 that even when the nuclei are the same, they absorb energy at different frequencies if the bonding positions within the molecule are different. That is, attention was payed after the discovery of the chemical shift phenomenon.

After this the development of the NMR technique was very rapid, and a high-resolution proton NMR instrument became commercially available in 1953.

With regard to ^{13}C-NMR, although there are many difficulties when compared to protons like the low natural abundance of ^{13}C and its low sensitivity, these difficulties were overcome when the FT (Fourier Transform)-NMR instrument became commercially available around 1970.

At present, because of the appearance of high-resolution instruments, besides proton and ^{13}C, NMR measurements are also possible for other nuclei. Also, NMR is quite freqeuntly used in medicine to obtain cross-sectional images of human organs.

4.2 Principles and Properties of NMR

Like the needle of a compass which is oriented in the south-north direction according to the magnetism of the earth, it is well known that when small magnets are placed in a strong magnetic field, the N and S poles

of these magnets orient themselves in a certain direction. Let us examine these magnets from the micro viewpoint. When a current is passed through a conducting wire, a magnetic field is produced around the wire. In other words, the electrical current is the flow of electrons with negative charges. That is, the magnets are produced by the action of electrons.

Next, let us consider the atom. An atom is composed of a nucleus containing positively-charged protons and neutral neutrons, and orbiting around the nucleus are negatively-charged electrons. Then the positive charge of the nucleus and the negative charge of the electrons are in balance to form a neutral species. Furthermore, like the case of the He atom (Figure 9), when 2 electrons orbit as a pair in an orbital, the magnetism of each electron is neutralized by the other, and no magnetic character is observed externally. As in the H atom (Figure 10), when there is an unpaired electron, it exhibits the properties of a magnet because the magnetism is not neutralized. In the case of the nucleus, because the positively charged particles are in motion, they exhibit magnetic properties. Similar to the case of electrons, in the nucleus as well, the protons and neutrons pair up with their own kind, and so a nucleus with an even number of protons and neutrons does not have magnetic properties (nuclear magnetic moments). Therefore, a nucleus with an odd number of both protons and neutrons, or with one of them an odd number, has a magnetic moment, and can be treated as a small magnet.

When a molecule containing an atom which possesses such a magnetic p.32
moment is placed in a magnetic field, the nuclear magnet formed by the nucleus attempts to orient itself in the direction of the magnetic field. However, because the molecules are in motion, not all the nuclei are oriented in the direction of the magnetic field, but instead the number of

nuclei oriented in the direction of the magnetic field is greater than those which are oriented in the opposite direction. Also, when placed in a magnetic field, the magnetic moment moves at a certain velocity due to the effects of the external magnetic field. When an external electromagnetic wave frequency is applied which is the same as this motion frequency, the magnetic moment motion and the electromagnetic wave are in resonance, and the magnetic moment of the nucleus absorbs the energy of that electromagnetic wave. This is the nuclear magnetic resonance phenomenon, and because the applied electromagnetic wave is changed by absorptions, resonance signals can be observed.

Further details on the theory of NMR can be obtained from the references.[16,69-71]

The spectrum obtained is called an NMR spectrum, which shows chemical shift values (δ) [ppm] on the horizontal axis and strength or intensity values on the vertical axis.

The chemical shift can be explained as follows. Even if the nuclei are of the same type, because the state of the electrons around each nucleus is different due to the types of atom bonds in the molecule, and because the magnetic effects from neighboring atoms change with the molecular structure, the actual magnetic fields experienced by the nuclei differ by a small amount. Because of this, even when the nuclei are the same the resonance frequencies are somewhat different. This difference is called the chemical shift. Therefore, when an NMR spectrum is measured, an externally applied magnetic field or the resonance frequencies are scanned, and one after another the signals are observed. In general, tetramethylsilane (TMS; $(CH_3)_4Si$) is used as the reference material, and

the differences for the frequencies from the instrument oscillator are expressed in ppm.

This section will describe ^{1}H and ^{13}C, the 2 most analyzed nucleuses.

Using ^{1}H NMR, the following can be determined: from the chemical shift values, the type of bond for each hydrogen in the molecule; from the intensity of the signals, the relative number of each type of hydrogen; and from the splitting of the signals, the positional relationship of each hyrogen. In this manner the following can be ascertained.

(1) By comparison with the spectra of known compounds, the identification and confirmation of a compound can be carried out.

(2) The molecular structure can be postulated.

This is particularly useful for carbon skeletons (branched or rings), carbon multiple bonds, isomers, stereochemistry, etc. However, one cannot readily determine the structure from the NMR spectrum alone, but MS or IR, etc. should also be used.

(3) The quantitative analysis of mixtures can be carried out.

(4) By using specific measuring techniques, a wide range of applications is possible.

In particular, one can obtain considerable information which are normally difficult to determine such as on reaction intermediates, *stereo*-structures, changes in bonding with temperature and solvent, etc.

^{13}C NMR is used in almost the same manner as ^{1}H NMR, but there are features and properties such as the direct information on the carbon skeletons can be obtained, weak signals can be detected by accumulation of signals, etc. When ^{13}C NMR is used along with ^{1}H NMR, it is very useful in the following cases.

(1) For compounds with long methylene chains or functional groups containg carbon.

(2) For polymers (analyses of stereo-regularity or oligomers).

(3) Natural products (complex structures or stereochemistry of structures).

(4) Reaction intermediates, unstable ions, radicals, etc.

Also, similar to the IR case, information on the structure and properties of the substance can be obtained without destruction of the sample.

4.3 The NMR Instrument

The methods used in detecting the resonance frequency waves in NMR are the CW (continuous wave) method which has been in use for a long time and the recently developed FT method. The CW method is one in which the magnetic field is continuously scanned, while in the FT method the signals are obtained by irradiating with pulses of high-frequency waves and then Fourier transformed. The FT method was developed as a result of the rapid advances in Fourier Transform techniques and in computers, and because the time taken for a one-pulse measurement is very short (0.1 to a few seconds), the accumulation efficiency is very good and has made possible extremely high-sensitivity measurements. When compared to the cost of a CW type instrument, an FT-NMR instrument is quite expensive, but because is has become very practical and convenient, it is now widely used.

Figure 11 shows the basic makeup of an FT-NMR instrument. The main components of an FT-NMR instrument are a magnet section, a high-frequency wave pulse generator and irradiation section, a detector and a computer.

The continuous wave generated at the high-frequency oscillator is transformed into a pulse wave at the gate using a direct-current pulse from the pulse generator, and then it is sent to the probe (detector). The

interference wave thus generated is picked up by the detector and converted to digital values by the A/D converter, and then sampling is carried out. These are accumulated and Fourier transformed with a computer to produce the NMR spectrum.

The performance of the NMR instrument is largely dependent on the strength of the magnet, that is, the stronger the magnetic field, the greater the resolution that can be obtained, which leads to greater sensitivity. Recently, with the developments in superconductors, instruments with magnetic fields stronger than ordinary permanent magnets or electromagnets have become possible, and so instruments with strong magnetic fields such as 200 MHz and 300 MHz are widely available. More recently, 400 MHz and 500 MHz instruments have appeared.

4.4 NMR Spectra p.33

4.4.1 ^{1}H NMR Spectra

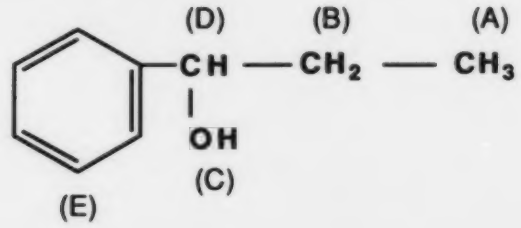
Figure 12 shows the ^{1}H NMR spectrum of a given compound.[72] As previously described, the resonance frequency value of each ^{1}H in the molecule is shifted from the others because of the effects of the unique surrounding magnetic environment of each type of ^{1}H. This chemical shift is a useful tool for determining the molecular structure. Figure 13 lists the main chemical shifts for ^{1}H.

^{1}H which have the same positional relationship in a molecule are considered to be equivalent; these exhibit the same resonance frequency value, and generally a one peak signal results. However, if they interact with other neighboring nuclei, splittings occur to give multiple peaks. This is called spin-spin coupling or spin coupling, with the distance between peaks given in Hz, which is called the spin coupling constant (J).

Table 7 shows a summary of spin-spin coupling. Table 8 shows the main spin coupling constant values.

Also, in ^{1}H NMR, an integration curve is used to obtain an area ratio of each of the signals, and when these area ratios are converted to whole numbers, the number of equivalent ^{1}H's of each type can be obtained.

When the NMR spectrum of Figure 12 is interpreted by taking into consideration the above discussion, it can be deduced that signal (A) is a methyl connected to a methylene, signal (B) is a methylene connected to a methyl and a methine, signal (C) is a hydroxyl, signal (D) is a methine, and signal (E) is a mono-substituted aromatic ring. Therefore, the compound of Figure 12 is postulated to be the following.



In addition, the references[16,73-76] can be consulted for methods of interpretation.

4.4.2 ^{13}C NMR Spectra

The ^{13}C spectrum also shows the chemical shifts on the horizontal axis and the relative strengths on the vertical axis. For the ^{1}H NMR case, the signals appear in the 0-10 ppm range, but for ^{13}C NMR, because the signals appear over a very wide range of 0 to about 250 ppm, there is very little overlap of the peaks, and even for a complex compound the number of signals observed corresponds to the number of carbons in the compound. Figure 14 shows a list of the main ^{13}C chemical shifts.

p.34

In general the ^{13}C NMR spectra do not show multiplet peaks. However, when special techniques are used for the measurement, multiplet peaks can be obtained, and these can be readily interpreted because the spin couplings occur only with the ^{1}H which are directly bonded to that carbon.

Also, although the integration curves do not give accurate integrated values, even for this aspect, if special measurement techniques are used, quantitative signal intensities can be obtained.

4.5 Other Special Measurement Methods

4.5.1 NMR of Other Nuclei[77)]

The magnetic resonance nuclei which are measured relatively easily and used often in chemical research are ^{1}H, ^{13}C, (^{15}N), ^{19}F, ^{31}P. For convenience, nuclei other than the above are called "other nuclei".

Because of the development of FT-NMR, the NMR measurements of these other nuclei have become possible. At present, ^{17}O, ^{29}Si, ^{35}Cl, ^{59}Fe, etc. are being used.

4.5.2 Solid High-Resolution NMR[78)]

The need for the direct NMR measurement of solids arose because of the desire to carry out the analysis of solid samples for which no suitable solvent could be found, the analysis of surface adsorption on solid materials, or to study chemical reactions on surfaces, etc. Because of the development of a special technique called Cross Polarization - Magic Angle Spinning (CP MAS)[79)] for solid samples, which uses high-frequencies waves and high-speed spinning, high-resolution spectra of solids became attainable. Solid high-resolution NMR instruments are in use at present for a wide range of solid samples such as high-molecular-weight substances, carbon materials, inorganic catalysts, etc.

Also, recently an NMR imaging method has been developed which can carry out measurements on human tissue in their normal state to provide sectional images; this method is called NMR-CT and is beginning to be seen as a powerful tool in clinical diagnosis. The characteristics of this NMR-CT method make it safer than the ordinary X-ray method because there are no harmful effects on living cells. p.35

4.5.3 Two-Dimensional NMR[71,81]

The characteristic of two-dimensional NMR is that, for NMR parameters such as chemical shifts and spin coupling constants, the NMR signals are developed and expressed in two dimensions. Thus, in this way resonance signals which are overlapped in the one-dimensional spectrum can be separated, as well as showing the mutual interactions among the spins of the resonating nuclei.

4.6 Applications to the Petroleum Industry

^{1}H NMR is being used as a substitute method for the hydrogen analyzer[82] or the FIA method for gasoline.[83] In the first case, calibration curves prepared from standard materials of known hydrogen content are used, and rapid quantitative determinations of hydrogen content in various petroleum samples such as airplane fuel, etc. can be carried out. In the latter case, the empirical formulae obtained for the various types are used, and from the ^{1}H NMR data, rapid quantitative determinations of saturates, olefins and aromatics in gasoline can be carried out.

Also, in the coal and petroleum related areas, it can be used in cases in which the normal analytical methods such as GC, HPLC, MS, etc. cannot be used to determine the various structural parameters where the structures of tar and pitch, etc. are composed of various types of mixtures with complex structures; that is, one can obtain the aromatic index

expressing aromaticity, the condensation index expressing the degree of aromatic ring condensation, the substitutionindex expressing the ratio of substitution on the aromatic rings, etc., and NMR is demonstrating its power in normal structural analyses.[84)]

5. Conclusions

The principles of MS, IR an NMR have been described above.

For qualitative analyses using these analytical methods, the commercially available spectral data are often used. However, because the spectral patterns can vary according to the measurement conditions, etc., in many cases the available commercial data are not satisfactory. Therefore, in many instances organizations prepare their own spectral data banks, and then use them for qualitative analyses.

These analytical methods, which were once regarded as high-level special measurement methods, have rapidly developed and now they have become routine and necessary methods, and the attention they are getting is similar to that when instrumental analytical methods were just beginning.

In the future there will likely be a wider range of applications for these analytical methods, and also the development of new methods which combine with new peripheral systems is expected.

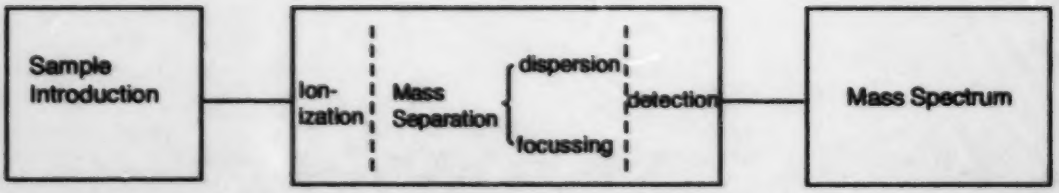


Figure 1. Flow Chart of MS

Table 1. The Main Ionization Methods

Ionization Method	Structure of Ion Source	Principle	Characteristics	Applications
EI (Electron Impact)	focus sample gas electron current filament	a single electron is ejected from a sample molecule (gas) for ionization $M \rightarrow (M)^{+} + e$	-Many fragment ions can be observed. -Structure can be deduced from the fragmentation pattern. -Operation is simple, reproducibility is good, and used most often.	general organic compounds
CI (Chemical Ionization)	reaction gas + sample gas electron current filament	Certain ions produced from the reaction gas (methane, etc.) by the electron current collide with the sample, and produce mainly protonated molecular ions. $M + CH_5^{+} \rightarrow (MH)^{+} + CH_4$	-Reaction gas containing about 1% sample is introduced to the ion source. -There are fewer fragment peaks (compared to EI). -100 times more sensitive than EI.	compounds in which parent ions are difficult to obtain by EI
FI (Field Ionization)	cathode emitter (anode) sample gas	When a high electric field is aplied, electrons from the sample near the anode migrate toward the emitter without molecular excitation to produce ionization $M \rightarrow (M)^{+}, \{(MH)^{+}\}$	-There are fewer fragment ion peaks. -Because the differences in sensitivities due to molecular structure among the parent ion peaks is small, quantitative determinations of complex mixtures is possible. -Sample amount required is more than 10 times that in the EI method.	Complex Mixtures
FD (Field Desorption)	cathode sample emitter (anode)	Sample directly applied to the emitter is ionized by the electrons being attracted to the emitter because of the localized high electric field. $M \rightarrow (M)^{+}, \{(MH)^{+}\}$	-Sample is directly applied to the emitter, solvent is removed and ionization occurs. -Very few fragment ion peaks are produced. -Highly polar samples tend to produce $(MH)^{+}$ due to proton transfer from the solvent. -Difficult to carry out quantitative determinations.	Non-volatile compounds Unstable componds
SIMS (Secondary Ion Mass Spectroscopy)	sample Ar^{+} sample phase	Ionization is produced by collision of the high-energy primary ions (Ar^{+}, etc.) with the surface where the sample is applied. $M \rightarrow (M)^{+}, \{(MH)^{+}\}$	-Sample solution is applied to silver plates, etc., and used for ionization. -More fragment ions than the FD method, and important information on molecular structures can be obtained.	
FAB (Fast Atom Bombardment)	sample Ar^{+} sample phase	Sample ionization is produced by collision of high-speed neutral atoms (Ar, etc.) with the applied sample phase. $M \rightarrow (M)^{+}, \{(MH)^{+}\}$	-In the SIMS method the samples tend to be charged and are difficult to ionize, but in the FAB method this is avoided by using a neutral atoms current	

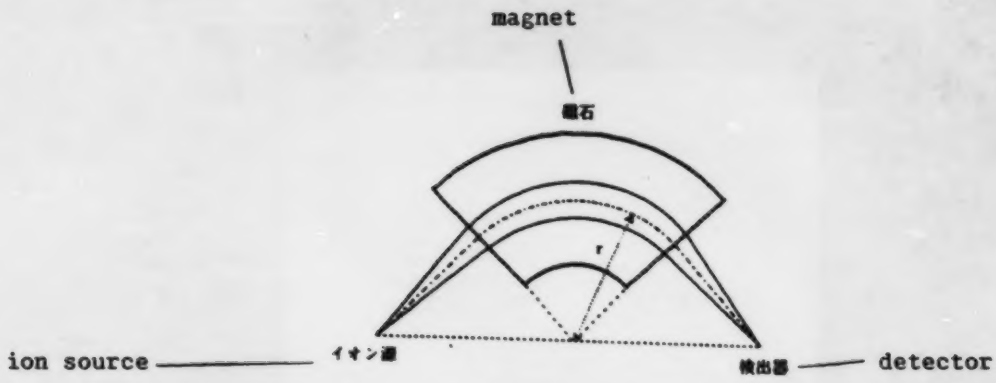


図2 単収束型質量分析計の概念図

Figure 2. Schematic Diagram of a Single Focussing Mass Spectrometer

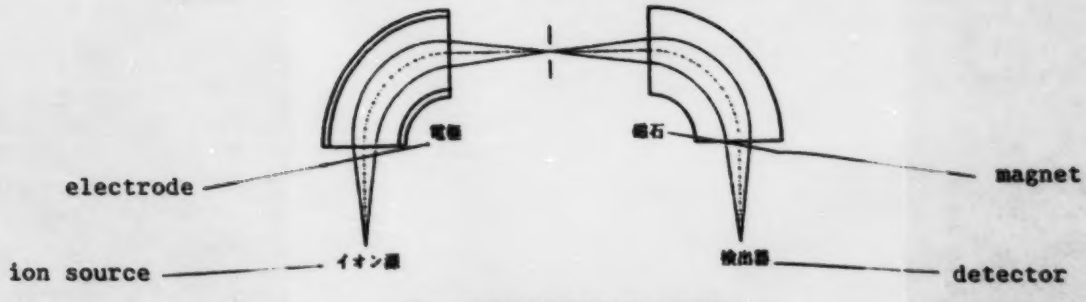


図3 二重収束型質量分析計の概念図

Figure 3. Schematic Diagram of a Double Focussing Mass Spectrometer

Table 2. Isotope Ratios of the Main Elements

表2 主な元素の同位体存在比

Isotopes and their abundances

同位体およびその存在量

element 元素名	M	M+1	M+2
hydrogen 水素	^{1}H 100	^{2}H 0.015	–
carbon 炭素	^{12}C 100	^{13}C 1.11	–
nitrogen 窒素	^{14}N 100	^{15}N 0.367	–
oxygen 酸素	^{16}O 100	^{17}O 0.038	^{18}O 0.200
fluorine フッ素	^{19}F 100	–	–
silicon ケイ素	^{28}Si 100	^{29}Si 5.06	^{30}Si 3.36
phosphorus リン	^{31}P 100	–	–
sulfur 硫黄	^{32}S 100	^{33}S 0.79	^{34}S 4.43
chlorine 塩素	^{35}Cl 100	–	^{37}Cl 31.98
bromine 臭素	^{79}Br 100	–	^{81}Br 97.28
iodine ヨウ素	^{127}I 100	–	–

most abundant isotope given a value of 100 and values given in %

存在量最大の同位体を100として%で表す

Table 3. m/z Values and Their Relative Strengths for the Mass Spectrum of a Compound

表3 ある試料の質量スペクトルの m/z と相対強度比

m/z	92	93	94
relative strength 相対強度比	100	7.5	0.2

Table 4. Relative Ratios of M+1 and M+2 for a Molecule with M=92

表4 M=92の分子式のM+1, M+2の相対比率

molecular formula 分子式	M+1	M+2
$CH_4N_2O_2$	2.02	0.61
CH_6N_4O	2.74	0.23
$C_2H_4O_3$	2.43	0.82
$C_2H_6N_2O_2$	3.15	0.44
$C_3H_4O_2$	3.56	0.64
$C_3H_6N_4$	6.34	0.17
C_4H_4O	6.76	0.39
C_7H_8	7.89	0.27

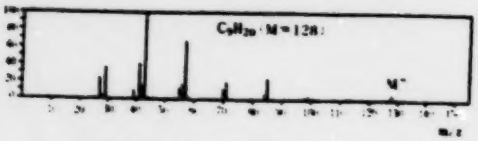


図4 n-ノナンの質量スペクトル

Figure 4. Mass Spectrum of n-nonane

Table 5. The Main Types of LC/MS Interfaces

表5 主なLC／MSインターフェースの型式

interface type インターフェースの型式	example 例
non-condensing direct insertion type 非凝縮直接導入型	脱溶媒室法、サーモスプレー法など solvent removing chamber method[22], thermo-spray method[23], etc.
condensing direct insertion type 凝縮直接導入型	レーザー法、エンリッチャー法など laser method[23], enricher method[25,26], etc.
belt type ベルト型	移動ベルト法、固定ワイヤー法 moving belt method[27], fixed wire method[28]
frit type フリット型	フリットFAB法 frit-FAB method[29-33]

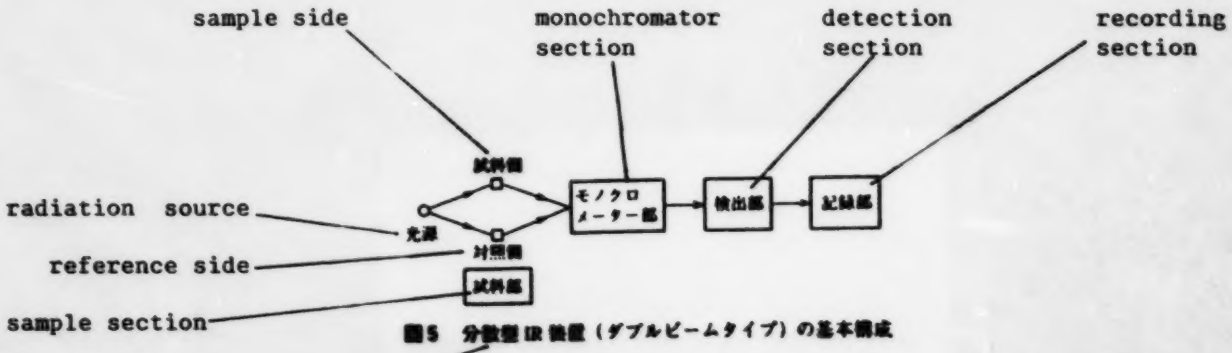


図5 分散型IR装置（ダブルビームタイプ）の基本構成

Figure 5. Basic Composition of the Dispersion Type IR Instrument (Double Beam Type)

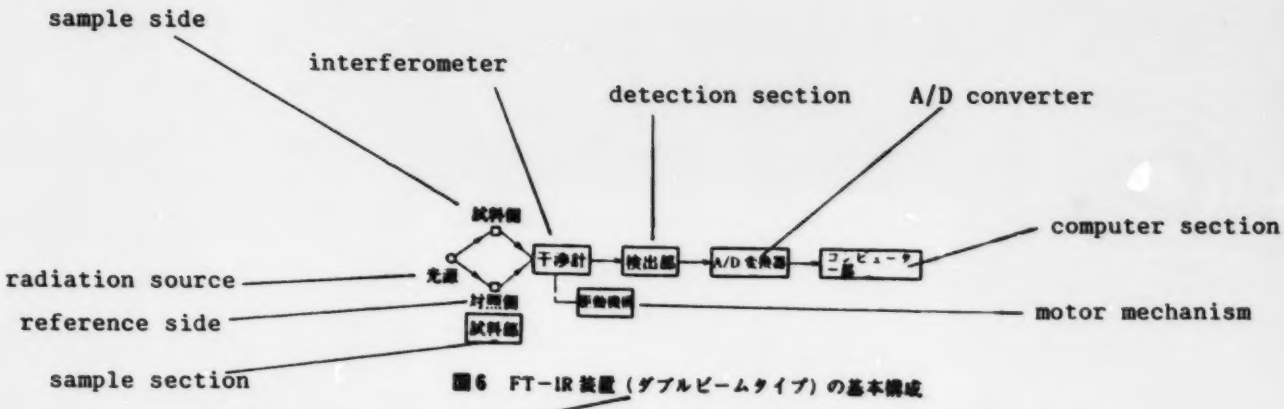


図6 FT-IR 装置（ダブルビームタイプ）の基本構成

Figure 6. The Basic Components of an FT-IR Instrument (double beam type)

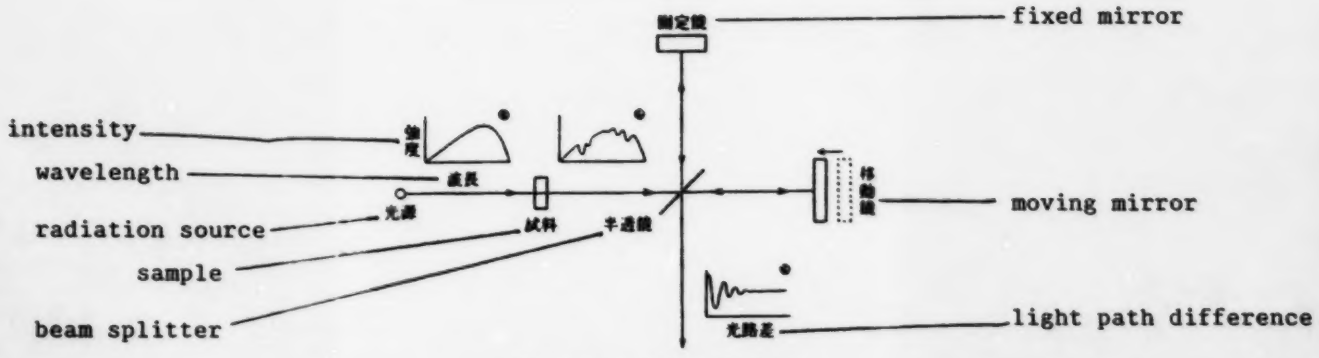


図7 光源から干渉計までの概略図

Figure 7. Schematic Diagram of Radiation Source to Interferometer

Table 6. The Major Methods of IR Measurement

Method of Measurement	Equipment	Sample	Characteristics
Liquid film method	assembled cell	low-volatility liquids (boiling points above 80°C)	Quantitative determinations can be readily carried out.
Solution method	fixed cell	high-volatility liquids (boiling points below 80°C)	Film thickness can be made constant, and can also be used for quantitative determinations.
Nujol method	assembled cell	solids (crushed)	Used for simple measurement of solids.
KBr method	pellet making device	solids (crushed)	Standard method for measuring solids.
Reflectance method	reflectometer	thin films, surface-adhered samples	Good for samples with high reflectivity.
High-sensitivity reflectance method	reflectometer optical rotamer	thin films, surface-adhered samples	Used when reflectance method is not sensitive enough.
Total reflectance method (ATR)	ATR measuring device	thin films, surface-adhered samples, powders	Good for leather surfaces, etc., for powders, and aqueous solutions can also be used.
Dispersion reflectance method	Dispersion reflectometer	powders	Powders can be directly measured.
Microscopic method	microscope measuring device	small-sized samples	Very small 10-20 μ samples can be measured.
Gas cell method	gass cell	gases, highly-volatile liquids	Using a long light-path gas cell (40 m - 1 km), very rarefied gases can be meaured.
Film method	fixed frame	polymers	Used for polymers which can be made into films.
Fluorescence method	fluorescence measuring device	solids	Remote measurements can be carried out, and heating conditions of sample can be analyzed.
Photoacoustic spectroscopy method (PAS)	PA cell	solids	Used for samples which change when ground up or when under pressure.

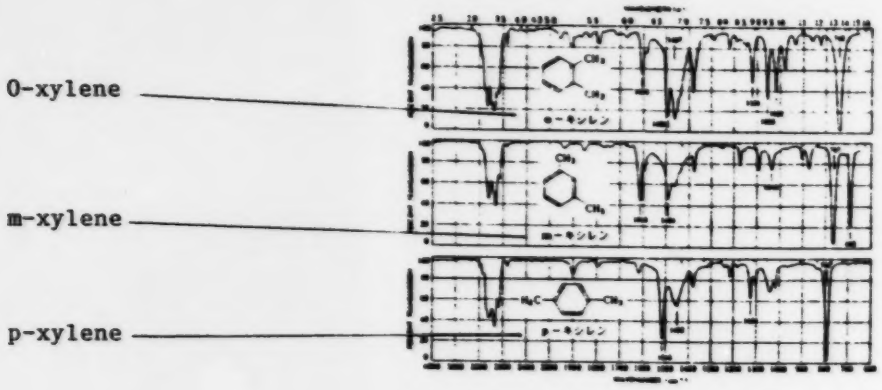


図8 o-, m-, p-キシレンの赤外スペクトル

Figure 8. Infrared Spectra of o-, m-, and p-Xylene

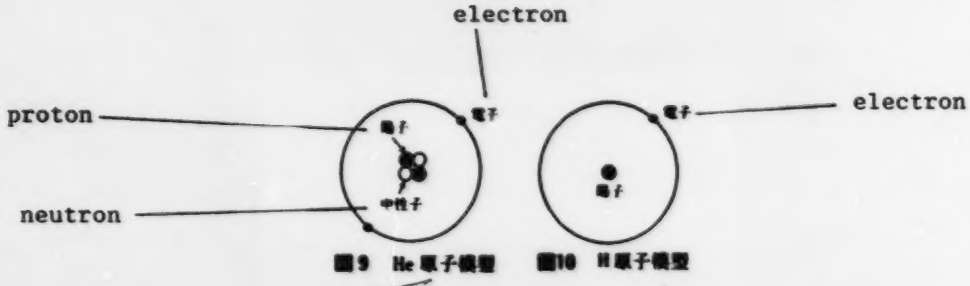


図9 He原子模型 図10 H原子模型

Figure 9. He Atom Model

Figure 10. H Atom Model

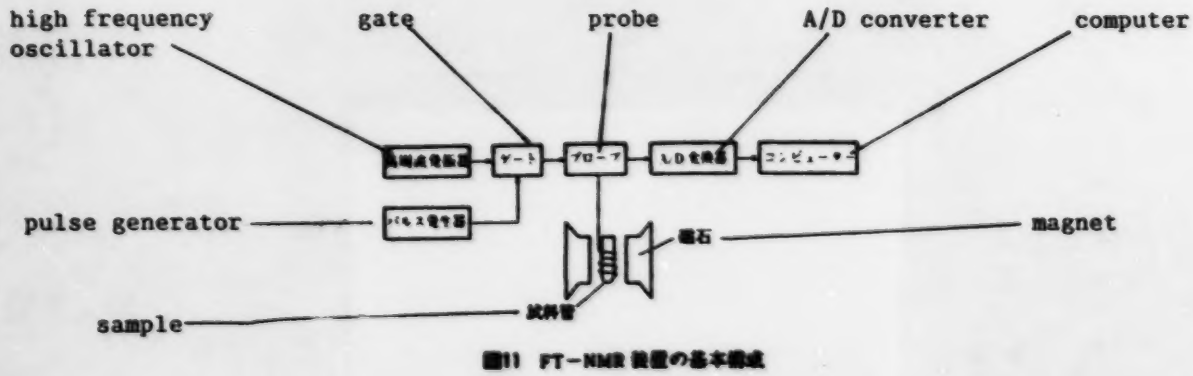


図11 FT-NMR装置の基本構成

Figure 11. Basic Components of an FT-NMR Instrument

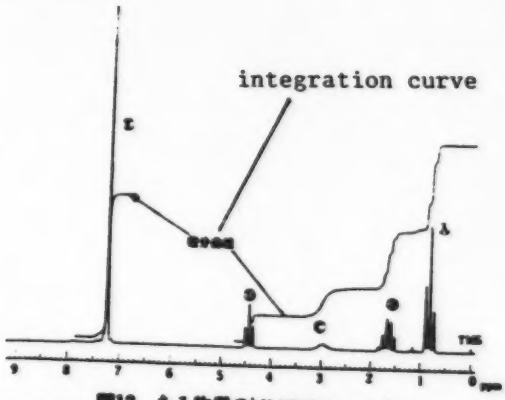


Figure 12. ^{1}H NMR Spectrum of a Compound

図12 ある物質の^{1}H NMR スペクトル

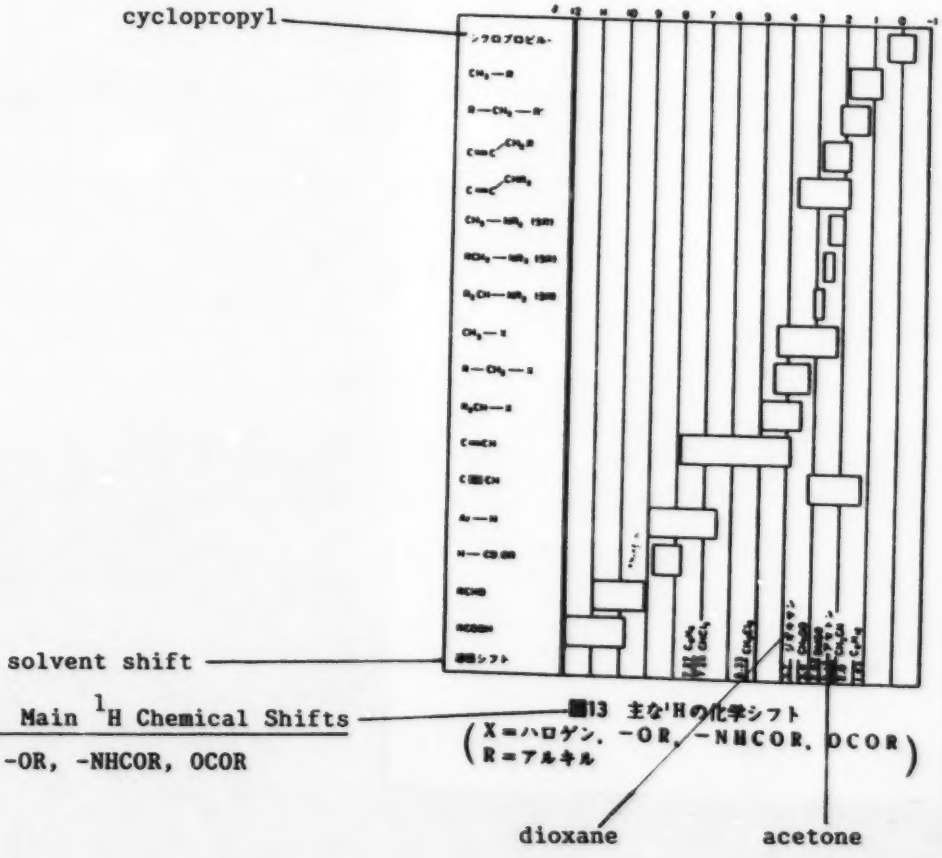


Figure 13. Main ^{1}H Chemical Shifts (X=halogen, -OR, -NHCOR, OCOR R=alkyl)

図13 主な^{1}Hの化学シフト (X＝ハロゲン，−OR，−NHCOR，OCOR R＝アルキル)

Table 7. Summary of Spin-Spin Coupling Constants

multiplet type (intensity ratio of multiplets)

multiplet

example (underlined ^1H)

表7 スピン-スピン結合の概要

分裂線	分裂線の形（分裂線の強度比）	例 （下線部の^1H）
singlet 一重線 singlet		$(C\underline{H}_3)_3-X$ $(C\underline{H}_3)_2-X$ $X-C\underline{H}_2-X$
doublet 二重線 doublet	(1 : 1)	$(CH_3)_2-C\underline{H}-X$ $C\underline{H}_3-CH-X_2$ $X-C\underline{H}_2-CH-X_2$
triplet 三重線 triplet	(1 : 2 : 1)	$C\underline{H}_2-CH_2-X$ $X_2-CH-C\underline{H}_2-CH-X$ $X-CH_2-C\underline{H}-X_2$
quartet 四重線 quartet	(1 : 3 : 3 : 1)	$CH_3-C\underline{H}_2-X$

Table 8. Main Spin Coupling Constants of ^1H

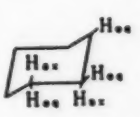
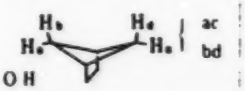
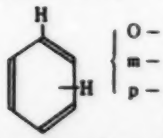
type of coupling

coupling constant (Hz)

type of coupling

coupling constant (Hz)

表8 主な^1Hのスピン結合定数

結合の形	結合定数（Hz）	結合の形	結合定数（Hz）
C H − C H	4.2~7.8	 1,2-	
C H = C H trans	14.5~16.5	ax ax	7.1~14.1
C H = C H cis	9.1~12.2	ax-eq	1.2~6.7
		eq-eq	2.0~3.0
C = C(H)(H)	0~±3.1	1,3-	
		eq-eq	1.0~2.0
C H − C = C − C H	0.8~1.6	 ac	7.0~8.0
C = C H − C H	5.0~11.4	bd	0
C H = C − C H	0~-2.5	C H − O H	4.6~8.5
C = C H − C H = C	10.4~12.5	C H − O − C H	0
		C = C H − O − C H	0.5
 O −	6.6~9.6	H O C − C H	0.8~3.0
m −	0~3.5		
p −	0~1.5	C H − N H	3.8~9.0
		C H − S H	5.8~12.0

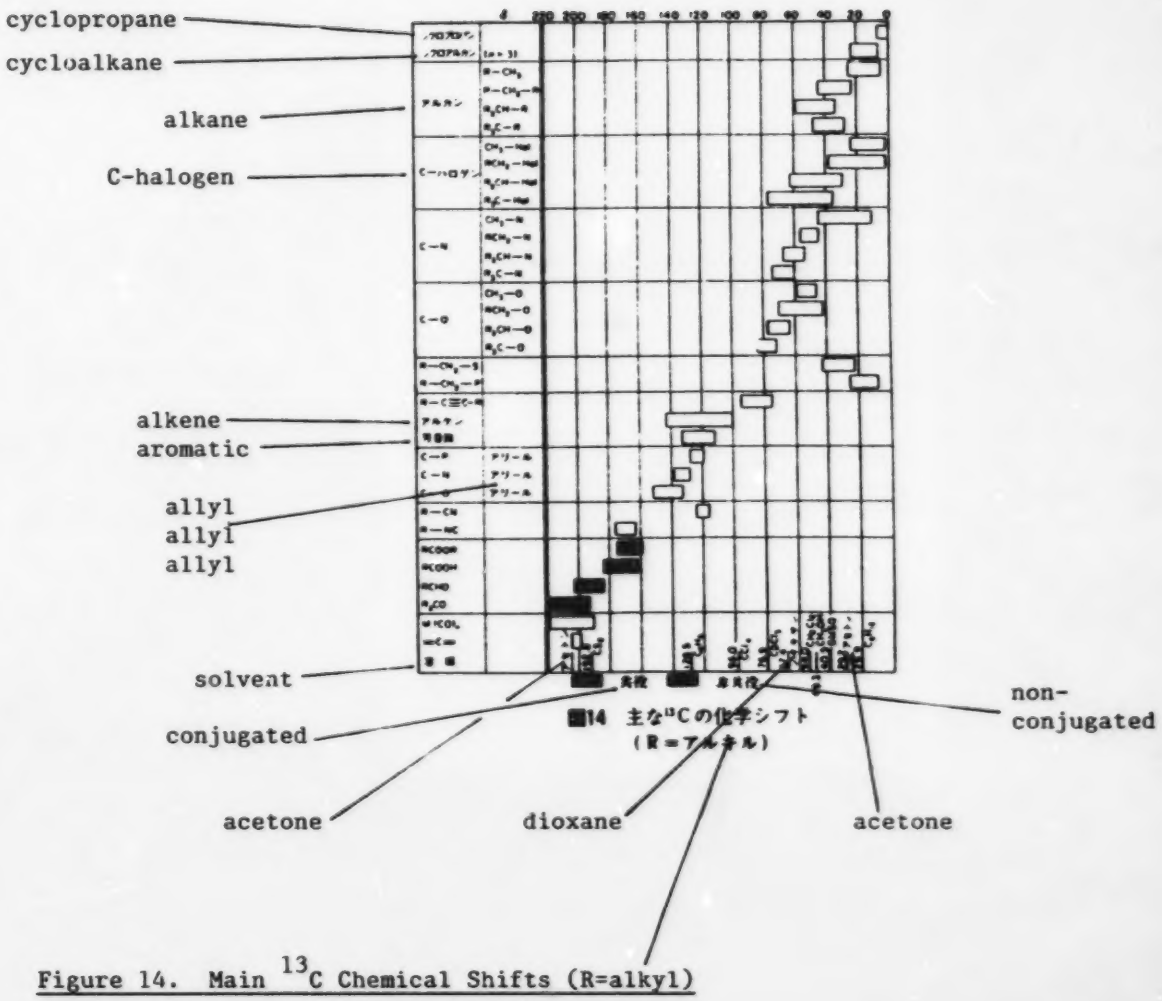


図14 主な^{13}Cの化学シフト
(R＝アルキル)

Figure 14. Main ^{13}C Chemical Shifts (R=alkyl)

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Information seulement

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